Solutions set for homework #3, Chem 130A Fall 2001

3.1 One mole of an ideal monatomic gas is expanded from an initial state at 2 atm and 400 K to a final state at 1 atm and 300 K.

(a) Choose two different paths for this expansion, specify them carefully, and calculate w and q for each path.

PATH I.

This path has two steps. In step A, the gas is cooled from 400 K to 300 K. In step B, the gas is isothermally compressed to 1 atm.

Step A: isochoric cooling

During isochoric processes, the volume remains constant. This greatly simplifies the calculation of work, as illustrated below:

$$w = -\int_{V_1}^{V_1} P \, dV = 0$$

As for heat, this is a constant-volume process for a monatomic ideal gas, hence

$$q = \int_{T_1}^{T_2} C_v \, dT = \frac{3}{2} R (T_2 - T_1) = \frac{3}{2}(8.31451 \ J \ mol^{-1} \ K^{-1})(300 \ K - 400 \ K) = -1.25 \ kJ$$

Step B: isothermal expansion (reversible)

As this process is isothermal, we know that
$$\Delta E = 0 \quad hence \quad q = -w$$

That's nifty, because all we have to do is to calculate work. Before we calculate work, we get to use the mighty Ideal Gas Law to calculate our starting and final volumes! Observe below to see the magic happen:

$$V_1 \ (at \ beginning \ of \ step \ B) = \frac{nRT_{initial}}{P_{initial}} = \frac{(1 \ mol)(0.082057 \ L \ atm \ K^{-1} \ mol^{-1})(400 \ K)}{(2 \ atm)} = 16.4 \ L$$

$$V_2 = \frac{nRT_{final}}{P_{final}} = \frac{(1 \ mol)(0.082057 \ L \ atm \ K^{-1} \ mol^{-1})(300 \ K)}{(1 \ atm)} = 24.6 \ L$$

$$w = -\int_{V_1}^{V_2} P dV = -nRT \int_{16.4 \ L}^{24.6 \ L} \frac{dV}{V} = -nRT \ln\left(\frac{V_2}{V_1}\right) = -(1 \ mol)(8.31451 \ J \ K^{-1} \ mol^{-1})(300 \ K) \ln\left(\frac{24.6 \ L}{16.4 \ L}\right)$$

$$= -1.01 \ kJ$$
$$q = 1.01 \ kJ$$

To calculate q and w for the entire path, we merely sum them over both sub-paths.

$$w_{Path\,I} = w_A + w_B = 0\ kJ - 1\ kJ = -1\ kJ$$

$$q_{Path\,I} = q_A + q_B = -1.25\ kJ + 1\ kJ = -0.25\ kJ$$

Path II.

With this path, step A is an isobaric cooling, and step B is an isothermal expansion.

Step A: isobaric cooling (reversible)

For a constant-pressure process, $q = q_p$.

$$q_P = n\overline{C_P}\Delta T = (1\ mol)\left(\frac{5}{2}R\right)(300\ K - 400\ K) = -2.08\ kJ$$

Calculation of work can proceed as follows:

$$w = -\int_{V_1}^{V_2} PdV = -P\int_{V_1}^{V_2} dV = -P\Delta V = -P(V_2 - V_1) = -P\left(\frac{nRT_2}{P} - \frac{nRT_1}{P}\right) = -nR(T_2 - T_1)$$

$$= -(1\ mol)(8.31451\ J\ K^{-1}\ mol^{-1})(300\ K - 400\ K) = 8.31\times10^{-1}\ kJ$$

Step B: isothermal expansion (reversible)

$$\Delta E = 0 \quad hence \quad q = -w$$

We can go ahead and solve for work, but we need to know what our initial and final volumes for step B are.

$$V_{1B} = \frac{nRT_{1B}}{P_{1B}} = \frac{(1\ mol)(0.080257\ L\ atm\ K^{-1}\ mol^{-1})(300\ K)}{2\ atm} = 12\ L$$

$$P_{1B}V_{1B} = P_{2B}V_{2B}$$

$$V_{2B} = \frac{P_{1B}V_{1B}}{P_{2B}} = \frac{(2\ atm)(12L)}{1\ atm} = 24\ L$$

$$w = -\int_{V_1}^{V_2} PdV = -nRT\int_{V_1}^{V_2}\frac{dV}{V} = -nRT\ \ln\left(\frac{V_2}{V_1}\right) = -(1\ mol)(8.31451\ J\ K^{-1}\ mol^{-1})(300\ K)\ln\left(\frac{24\ L}{12\ L}\right)$$

$$= -1.73\ kJ$$

$$q = 1.73\ kJ$$

Now we can solve for q and w for all of path II.

$$q_{tot} = q_A + q_B = -2.08\ kJ + 1.73\ kJ = -0.35\ kJ$$

$$w_{tot} = w_A + w_B = 0.83\ kJ + -1.73\ kJ = -0.90\ kJ$$

(b) Now calculate ΔE and ΔS for each path.

Path I:

$$\Delta E_I = q + w = -0.24\,kJ + (-1.01\,kJ) = -1.25\,kJ$$

$$\Delta S_I = \Delta S_a + \Delta S_b = \int_{T_1}^{T_2} \frac{dq_V}{T} dT + \frac{q_b}{T_b} = n\overline{C_V}\ln\frac{T_2}{T_1} + \frac{q_b}{T_b} = (1mol)\left(\frac{3}{2}\right)\left(8.3145\,J\ K^{-1}\ mol^{-1}\right)\ln\left(\frac{300K}{400K}\right) + \frac{1010J}{300\,K}$$

$$= -0.217J\ K^{-1}$$

Path II:

$$\Delta E_{II} = q + w = -0.35\,kJ + (-0.9\,kJ) = -1.25\,kJ$$

$$\Delta S_I = \Delta S_a + \Delta S_b = \int_{T_1}^{T_2} \frac{dq_P}{T} dT + \frac{q_b}{T_b} = n\overline{C_P}\ln\frac{T_2}{T_1} + \frac{q_b}{T_b} = (1mol)\left(\frac{5}{2}\right)\left(8.3145\,J\ K^{-1}\ mol^{-1}\right)\ln\left(\frac{300K}{400K}\right) + \frac{1730J}{300K}$$

$$= -0.217J\ K^{-1}$$

There are many, many other paths that you can choose. However, given that ΔE and ΔS are state functions, they should always end up being the same regardless of the path.

3.3 The second law of thermodynamics states that entropy increases for spontaneous processes and that an increase in entropy is associated with transitions from ordered to disordered states. Living organisms, even the simplest bacteria growing in cultures, appear to violate the second law because they grow and proliferate spontaneously. They convert simple chemical substances into the highly organized structure of their descendants. Write a critical evaluation of the proposition that living organisms contradict the second law. Be sure to state your conclusion clearly and to present detailed, reasoned arguments to support it.

Bacteria (and other living things) don't break the second law. There are two arguments behind this. Firstly, bacteria take in many relatively complex molecules (i.e. peptides, sugars) from the surrounding medium and break them down into multiple smaller molecules, e.g. CO_2 and H_2O. The metabolism of complex molecules increases entropy in this fashion.

Another factor to consider is that bacteria produce heat from the chemical energy contained in peptides, sugars, and other compounds. Heat is released to the surroundings of the bacteria (i.e. the medium in which they are growing) and the entropy of the surroundings is increased. Therefore, while the entropy of the bacteria may be negative, the sum of the entropies of the bacteria and their surroundings can be positive.

3.7 For the following processes, determine whether each of the thermodynamic quantities listed is greater than, equal to, or less than zero for the system described (the system is shown in italic type in each case). Consider all gases to

behave ideally. Indicate your reasoning and state explicitly any reasonable assumptions or approximations that you need to make.

(a) A sample of gas is carried through a complete Carnot cycle (isothermal expansion, adiabatic expansion, isothermal compression, and adiabatic compression—all reversible): ΔT, q, w, ΔH, ΔS, ΔE, and ΔG.

$\Delta T = 0$, because it is a cycle (return to the same temperature).
$\Delta H = \Delta S = \Delta E = \Delta G = 0$ because they are state functions and this is a cycle
$q > 0$ (overall, the Carnot engine takes in heat)
$w < 0$ (engine performs work on the surroundings)

(b) A sample of *hot water* is mixed with a sample of *cold water* in a thermally insulated, closed container of fixed volume: w, q, ΔE, ΔH, ΔS.

$q = 0$ (thermally insulated)
$w = 0$ (no volume change)
$\Delta E = q + w = 0$
$\Delta H = \Delta E + \Delta(PV) = 0$ (volume and pressure changes are very, very small)
$\Delta S > 0$ (spontaneous process)

(c) An ideal gas expands adiabatically and reversibly: ΔV, ΔT, w, q, ΔE, ΔH, ΔS

$\Delta V > 0$ (expansion)
$q = 0$ (adiabatic)
$w < 0$ (expansion)
$\Delta E = w < 0$
$\Delta T < 0$ because $\Delta E = nC_V\Delta T < 0$
$\Delta H = nC_P\Delta T < 0$
$\Delta S = 0$ (adiabatic and reversible)

(d) A flask of liquid nutrient solution inoculated with a small sample of bacteria is maintained for several days in a thermostat until the bacteria have multiplied 1000-fold: ΔT, w, q, ΔE, ΔH, ΔG

$\Delta T = 0$ (in a thermostat)
$q < 0$ (energy from nutrients turned into heat)
$w \approx 0$ (pressure and volume aren't really changing, unless the bacteria are gas-producing like some of the bacteria in our intestines)
$\Delta E \approx q < 0$
$\Delta H \approx \Delta E < 0$ (again, volume does not really change)
$\Delta G < 0$ (spontaneous)